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# Chemical Interaction of Mn With the MoS<sub>2</sub> (0001) Surface Studied by High-Resolution Photoelectron Spectroscopy

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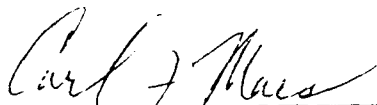
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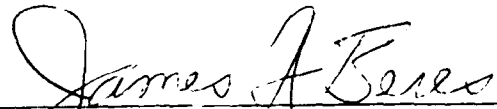
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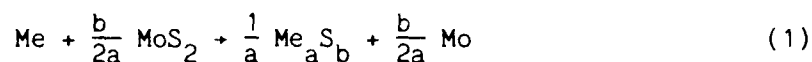
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## I. INTRODUCTION

The interaction of transition metals with  $\text{MoS}_2$  surfaces has been increasingly studied recently with respect to applications in catalysis,<sup>1</sup> electronics materials,<sup>2,3</sup> and tribology (lubrication).<sup>4</sup> Especially well studied is the chemistry at the metal/ $\text{MoS}_2$ (0001) interface. This surface of  $\text{MoS}_2$  is remarkable because of the highly anisotropic  $\text{MoS}_2$  crystal structure.  $\text{MoS}_2$  crystallizes in layers of S-Mo-S "sandwiches," within which the bonds are covalent, but each layer is bonded to the next one by relatively weak van der Waals' forces. As a result, its basal plane [or (0001)] surface, produced by cleaving between these layers, is relatively inert with respect to metal deposition.

The expected reaction of metals with  $\text{MoS}_2$  to form metal sulfides is as follows:



The free energy of reaction per metal atom (or  $\Delta G_{\text{rxn}}$ ) indicates that, at room temperature, a large number of metals are able to form sulfides based on bulk, equilibrium thermodynamics.<sup>2,3</sup> However, the work of McGovern, et al.,<sup>3</sup> Lince, et al.,<sup>2,4</sup> and Kamaratos, et al.,<sup>1,5,6</sup> indicates that, although a negative or small positive  $\Delta G_{\text{rxn}}$  is a necessary condition for chemical reaction in this system, it is not sufficient as an indicator of reactivity at room temperature. Of the metals studied that correspond to this thermodynamic condition (i.e., are expected to chemically react with  $\text{MoS}_2$ ), Al,<sup>2,3</sup> Cu,<sup>3</sup> In,<sup>2,3</sup> Pd,<sup>2,5</sup> and V<sup>2</sup> do not react, Fe<sup>1,4</sup> and Ni<sup>3</sup> exhibit minimal reactivity (Ni might be nonreactive),<sup>6</sup> and only Mg,<sup>2,3</sup> Ti,<sup>2,3</sup> and Mn<sup>2</sup> exhibit strong reactivity, i.e., decomposition of the substrate into metallic molybdenum and metal sulfide. Therefore, there are kinetic constraints in this system due to the structure of the individual metals in addition to the anisotropic structure of the  $\text{MoS}_2$ (0001) surface.

To investigate the chemistry of the more reactive interfaces in greater detail, we conducted a study of the interaction of thin films of Mn with the  $\text{MoS}_2(0001)$  surface. The techniques we used are (a) core level and valence band photoelectron spectroscopies excited by synchrotron radiation, and (b) low energy electron diffraction (LEED). The use of synchrotron radiation allows for control of the electron escape depth by varying the photon energy. In addition, the use of a small line-width monochromator and a high-resolution electron energy analyzer is shown to be necessary to correctly deconvolute the various species in the core level spectra, since binding energy shifts can be small during sulfide formation.

## II. EXPERIMENTAL

The present study was performed at beam line UV-8b at the National Synchrotron Light Source at Brookhaven National Laboratory. The sample preparation procedures,<sup>7</sup> electron spectrometer,<sup>8</sup> and monochromator<sup>9</sup> have been described previously. Briefly, clean basal plane [or (0001)] surfaces were produced by cleavage of natural molybdenite crystals in air, followed by annealing at -975 K for 10 min in the metal deposition chamber ( $\sim 1 \times 10^{-10}$  Torr base pressure). This annealing procedure is known to remove virtually all contamination from the surface without formation of defects.<sup>10,11</sup> Photoelectron spectra showed no evidence of either carbon, oxygen, or other impurities on the surface of the samples after the anneal, while LEED showed good quality (0001) -  $1 \times 1$  patterns. The sample preparation chamber was connected to the spectrometer chamber ( $\sim 3 \times 10^{-11}$  Torr base pressure), so that the samples could be kept in ultrahigh vacuum (UHV) during transfer between metal deposition and analysis steps.

The instrument resolution is demonstrated by the complete separation of the  $j = 1/2$  and  $j = 3/2$  components of the S-2p doublet for the cleaved  $\text{MoS}_2(0001)$  surface in Fig. 1e. The instrumental resolution was estimated to be 0.3 eV at 150-225 eV photon energy, and 0.4 eV at 290-300 eV photon energy. The S-2p and Mo-3d core levels were collected for  $h\nu = 230$  and 300 eV, respectively, corresponding to a -70 eV electron kinetic energy. This ensured that the same electron escape depth ( $\sim 4\text{\AA}$ )<sup>12</sup> was obtained for sampling both the S and the Mo. The Mn-3p and Mo-4p core level spectra were recorded for a photon energy of 290 eV (kinetic energies of -240 and -255 eV) while the valence band spectra were collected for photon energies of 152 and 224.7 eV (resulting in escape depths of  $\sim 5.5$  and  $\sim 6.5\text{\AA}$ , respectively). The spectra were normalized by dividing the photoelectron current by the photon intensity determined by measuring the total current resulting from the electron emission from the (carbon contaminated) Au-coated final focusing mirror with an electrometer.

Core level spectra were deconvoluted with Voigt functions using a peak fitting procedure.<sup>7</sup> The Mo-3d doublet was fit by constraining the peak separation and the branching ratio for the 5/2 and 3/2 spin-orbit components to be 3.14 eV and 1.43, respectively, while the corresponding constraints for the S-2p 3/2 and 1/2 spin-orbit components were 1.19 eV and 2.01. These values were derived from spectra for a number of clean MoS<sub>2</sub>(0001) surfaces (The branching ratios are different from the theoretical values of 1.50 and 2.00 due to final state effects.)

Manganese (99.995% purity) was evaporated onto the sample surface from a 1/4-in.-diameter tungsten wire basket at a rate of ~12 Å/min. The pressure during deposition was typically in the mid 10<sup>-10</sup> Torr range. The sample remained at ambient temperature during deposition. Mn film thicknesses were determined by measuring the deposition rate with a quartz crystal microbalance, which could be moved into the position where the sample is located during film growth. This procedure is accurate to within ~50%. After the deposition, and also after subsequent annealing, there was no evidence of carbon or oxygen detected by photoelectron spectroscopy.

The deposition of Mn and subsequent annealing was performed on two separate samples. The spectra displayed herein are from one sample, but are also representative of those for the other sample.

### III. RESULTS AND DISCUSSION

#### A. CORE LEVEL SPECTRA

Figure 2 shows the evolution of the Mn-3p and Mo-4p core levels deposition of Mn on MoS<sub>2</sub>(0001) and subsequent annealing. As the Mn is deposited, the Mn peak increases relative to the Mo peak. The Mn film has covered the MoS<sub>2</sub> substrate after deposition of 58 Å Mn (the Mo-4p is present in Fig. 2c, but is difficult to see because of the high relative intensity of the Mn-3p peak). The binding energy and the increased intensity on the high binding energy side of the Mn-3p peak for all coverages indicates that the Mn is primarily in the form of metallic Mn coexisting with a small amount of Mn in a higher oxidation state, possibly as a sulfide. Annealing the 58 Å film to progressively higher and higher temperatures results in reappearance of the Mo-4p peak caused by agglomeration of the Mn layer into islands, which uncovers the substrate. In addition the Mn-3p spectrum shifts -1.8 eV to higher binding energy with the first anneal, and exhibits a decrease in overall peak width. This shift is consistent with the formation of MnS, since the difference in the Mn-3p binding energies of Mn and MnS has been determined to be in the range of 1.6 eV<sup>13,14</sup> to 2.4 eV.<sup>15</sup> Therefore, the increase in temperature increased the rate of reaction, driving the reaction to equilibrium, which in this case corresponds to sulfide formation, consistent with the negative  $\Delta G_{\text{rxn}}$  mentioned above. After the anneals, the Mo-4p spectrum appears to have shifted to lower binding energy, indicating reduction of the Mo in the MoS<sub>2</sub>.

The various species in the Mo-3d and S-2p spectra were deconvoluted by curve fitting, and the results are shown in Fig. 1 for the clean surfaces and three of the depositions (22, 35, and 58 Å; the corresponding spectra for 10 and 50 Å are not shown for reasons of brevity, but their trends are similar to the spectra shown). Initial deposition of Mn caused the Mo-3d peak representing the Mo in the MoS<sub>2</sub> substrate [Mo in the +4 oxidation state, denoted "Mo(substrate)"] to shift -0.3 eV to lower binding energy

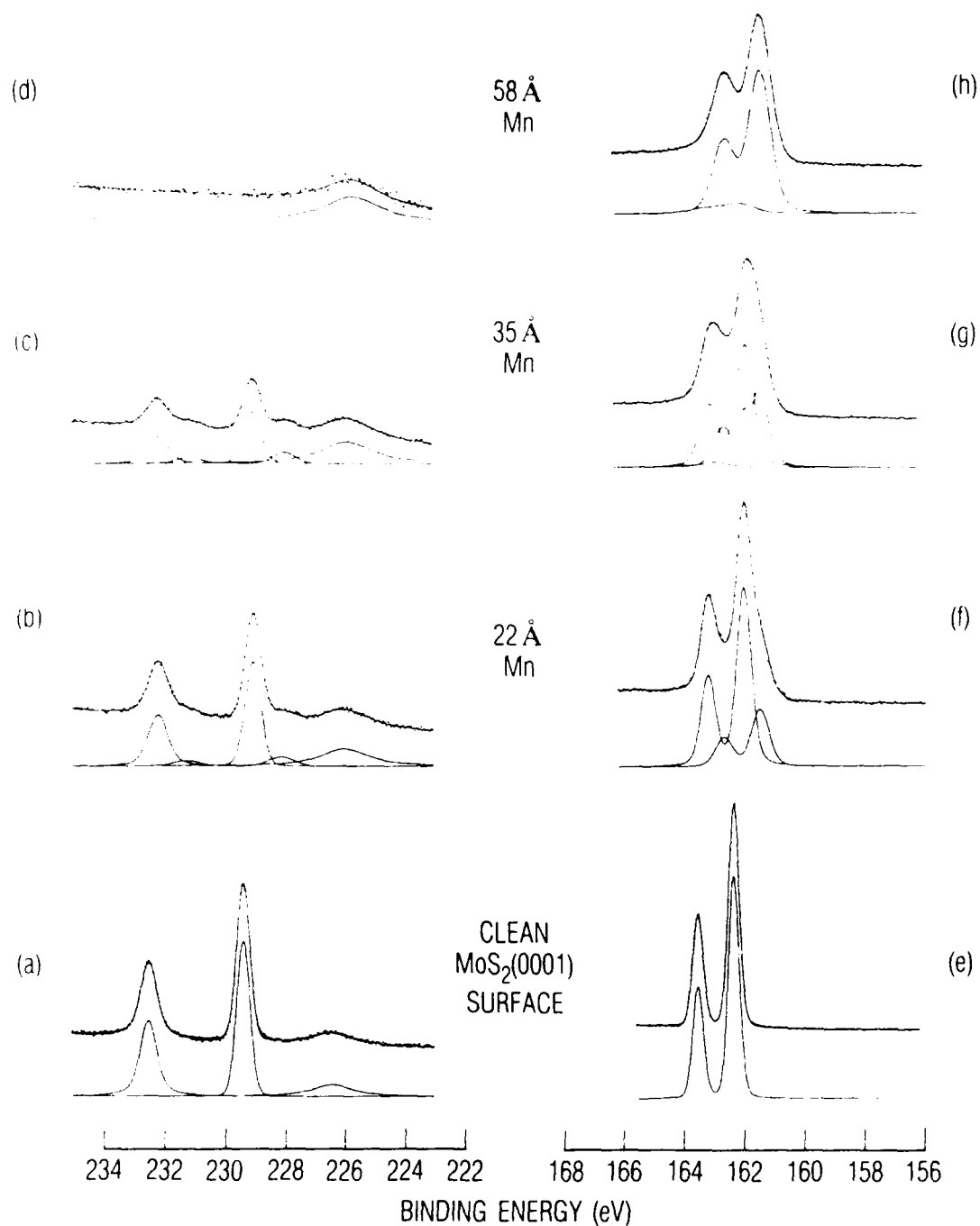


Fig. 1. Mo-3d (a-d) and S-2p (e-h) Core Level Spectra for Deposition of Mn on the  $\text{MoS}_2(0001)$  Surface. Spectra for the Mo-3d and S-2p core levels were taken with a photon energy of 300 and 230 eV, respectively, resulting in a photoelectron kinetic energy of  $\sim 70$  eV for both Mo and S photoelectrons. Spectra are shown for (a,e) the clean  $\text{MoS}_2(0001)$  surface, and after deposition of (b,f) 22 Å Mn, (c,g) 35 Å Mn, and (d,h) 58 Å Mn. The S-2p peak is at  $\sim 226$  eV in spectra a-d. Binding energies are relative to Fermi energy  $E_F$ .

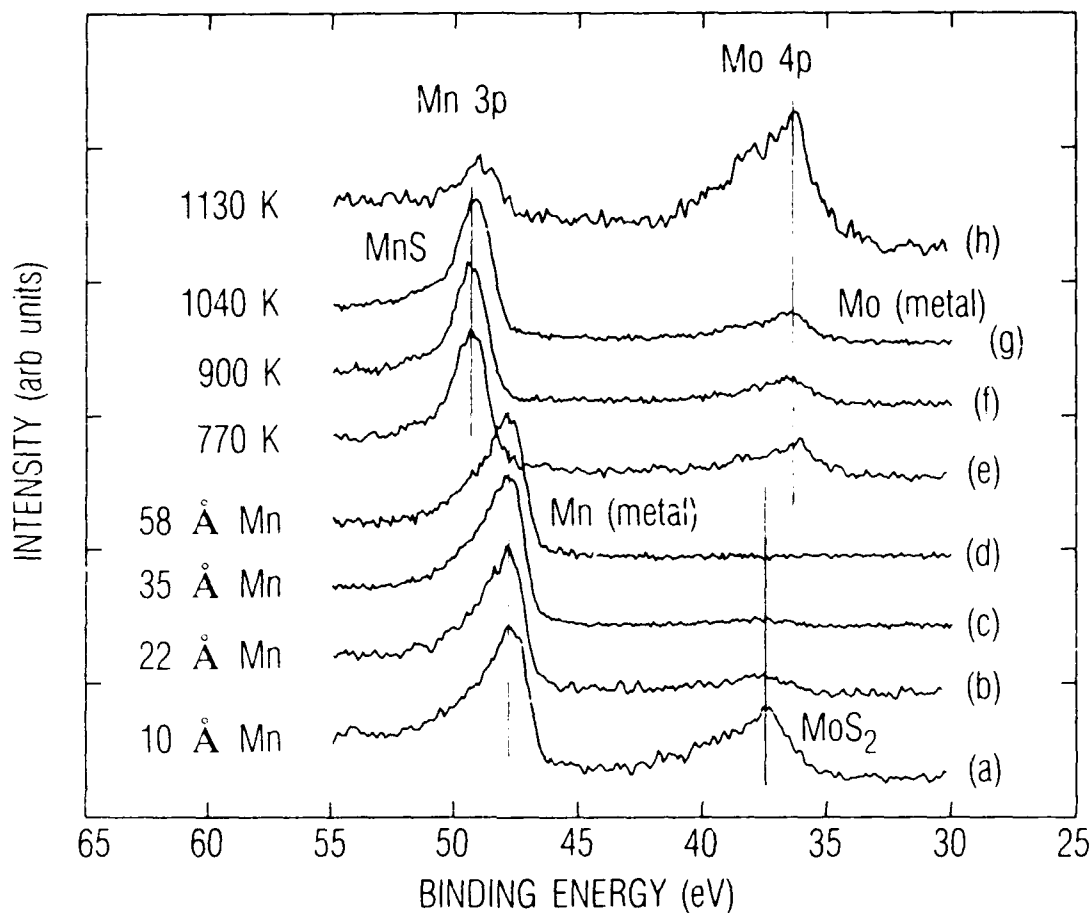


Fig. 2. Mn-3p and Mo-4p Core Level Spectra for Deposition and Annealing of Mn on the  $\text{MoS}_2(0001)$  Surface. Spectra were taken with a photon energy of 290 eV, resulting in kinetic energies of ~240 and ~255 eV for Mn and Mo photoelectrons, respectively. Spectra are shown for depositions of (a) 10 Å Mn, (b) 22 Å Mn, (c) 35 Å Mn, and (d) 58 Å Mn. Spectra for the 58 Å Mn film are shown after annealing to (e) 770 K, (f) 900 K, (g) 1040 K, and (h) 1130 K. Binding energies are relative to  $E_F$ .

due to band-bending (see Fig. 1b and Table I). Also, a reduced Mo species appears whose separation from the Mo(substrate) peak ( $\sim 1.0$  eV, see Table I) corresponds with the formation of metallic Mo [denoted Mo(metal)].<sup>13</sup> The S-2p spectrum deconvolutes clearly into two species (see Fig. 1f): the substrate S [denoted S(substrate) in Table I, and a lower-binding energy species show binding energy (BE) is consistent with that for MnS<sup>15,16</sup> [denoted S(MnS)]. The Mo(metal) peak and the S(MnS) peaks increase in area (relative to the substrate peaks, see Table II) with deposition up to 35 Å thickness (see Fig 1, spectra c and g). For the 58 Å deposition, Mo is not detectable above the noise level in the Mo-3d region (see Fig. 1d), and the S-2p peak exhibits mostly a broadened peak representing the MnS, with a small amount of intensity on the high binding energy side, possibly representing a small amount of S from the MoS<sub>2</sub> substrate (see Fig. 1h).

Table I. Binding Energies of Mo-3d and S-2p Core Levels on the MoS<sub>2</sub>(0001) Surface After Mn Deposition<sup>a</sup>

	Mo-3d		S-2p	
	BE	BE	BE	BE
	Mo(substrate)	Mo(metal)	S(substrate)	S(Mns)
Clean surface	229.4 eV	---	162.3	---
Average for 10, 22, and 35 Å Mn	229.07 ±.03	228.04 ±.08	161.93 ±.06	161.40
770 K anneal	228.45 ±.10	227.68	---	161.64
Average for 850, 900, 970 and 1040 K anneals	---	227.90 ±.05	---	161.55 ±.06
1130 K anneal	229.18	227.82	161.94 ±.05	161.25 ±.10

<sup>a</sup>Uncertainty in binding energies is  $\sim 0.02$  eV, unless otherwise stated.

Table II. Relative Areas of the Mo-3d and S-2p Peaks of the MoS<sub>2</sub>(0001) Surface After Mn Deposition

	$\frac{\text{Mo(metal)}}{\text{Mo(total)}}$	$\frac{\text{S(MnS)}}{\text{S(total)}}$	$\frac{\text{S(low)}^a}{\text{S(total)}}$	$\frac{\text{S(substrate)}}{\text{S(total)}}$	$\frac{\text{S(total)}^b}{\text{Mo(total)}}$
Clean surface	0%	0%	---	100%	1.00
Mn coverage					
10 Å	5%	12%	---	88%	1.01
22 Å	12%	15%	---	85%	2.54
35 Å	22%	38%	---	62%	2.99
58 Å	--- <sup>c</sup>	91%	---	9%	--- <sup>c</sup>
Anneal temp of 58 Å Mn film					
770 K	89%	75%	16%	9%	1.65
900 K	96%	93%	4%	-3%	2.10
1040 K	-100%	85%	11%	-0%	1.50
1130 K	67%	38%	6%	56%	0.74

<sup>a</sup>This ratio represents the "low binding energy" component of the S-2p spectrum, visible only in the annealed samples. The uncertainty in this ratio is -0.2 times the stated value.

<sup>b</sup>This ratio is expressed relative to the ratio for the clean surface, which is set arbitrarily to a value of 1.00. The uncertainty in the ratios is estimated to be 0.05.

<sup>c</sup>This ratio is undefined because no Mo-3d spectrum was detected for this coverage.

The core level results indicate that the Mn grows on MoS<sub>2</sub>(0001) in the Volmer-Weber growth mode<sup>17</sup> [three-dimensional (3D) island formation]. This is indicated by the need to deposit  $> 50$  Å Mn to cause the Mo-3d signal to disappear, much greater than the  $\sim 4$  Å escape depth for  $\sim 70$  eV electrons (see Section II). In addition, the Stranski-Krastanov growth mode<sup>18</sup> (growth of one or a few 2D layers followed by 3D island formation) can be ruled out, as the initial deposition of 10 Å Mn resulted in a drop of the Mo(substrate) and S(substrate) peak areas by less than 15% relative to the clean surface. The LEED pattern of the sample does not indicate the

presence of an ordered overlayer film, since deposition of 10, 22, and 35 Å Mn causes an increase in background intensity of the (0001) -  $1 \times 1$  pattern, while for dispositions of 50 and 58 Å Mn, and anneals of 770-1040 K, no pattern is seen at all.

After annealing the 58 Å film to 770 K, the Mo-3d spectrum reappears (see Fig. 3b). This deconvolutes into two doublets. The larger one corresponds to the binding energy for metallic Mo,<sup>13</sup> although it is -0.2 eV less than for the subsequent anneals to 850 - 1040 K. The smaller doublet corresponds well to MoS<sub>2</sub> with S vacancy defects, or MoS<sub>2-x</sub>, where  $0 < x < 1$ .<sup>7</sup> The S-2p doublet (see Fig. 3f) represents mainly MnS, but exhibits a small amount of intensity on the high binding energy side, possibly corresponding to S in the MoS<sub>2-x</sub> region of the surface, and a lower binding energy species. This lower binding energy species [denoted S(low) in Table II] might represent another sulfide of Mn. It also might represent S adsorbed on the surface of either the Mo(metal) or the MnS. (The adsorption of S on Mo(0001) has been shown to exhibit a lower S-2p binding energy than S in MoS<sub>2</sub>.<sup>7,19</sup>) When the sample is annealed to higher temperatures, i.e., to 850 and 900 K, the substrate components in both the Mo-3d and S-2p spectra decrease (see Table II), and have disappeared after the anneal to 970 and 1040 K (see Table II and Fig. 3, spectra c and g). This indicates that the reaction to form MnS has been driven by the increase in temperature, in agreement with the Mn-3p core level results (see Fig. 2, spectra d through g). The decrease in the area of the S(low) doublet at 850 K and 900 K is concurrent with the rise in the S(total):Mo(total) ratio, while the subsequent rise in S(low) at 970 K and 1040 K is concurrent with the fall of the S(total):Mo(total) ratio. The amount of Mo(total) is virtually equal to the amount of Mo(metal) during annealing. Therefore, a change in the amount of S(low) seems to move in the same direction as a change in the amount of Mo(metal). This is consistent with the conclusion that the S(low) species represents S adsorbed on the Mo(metal).

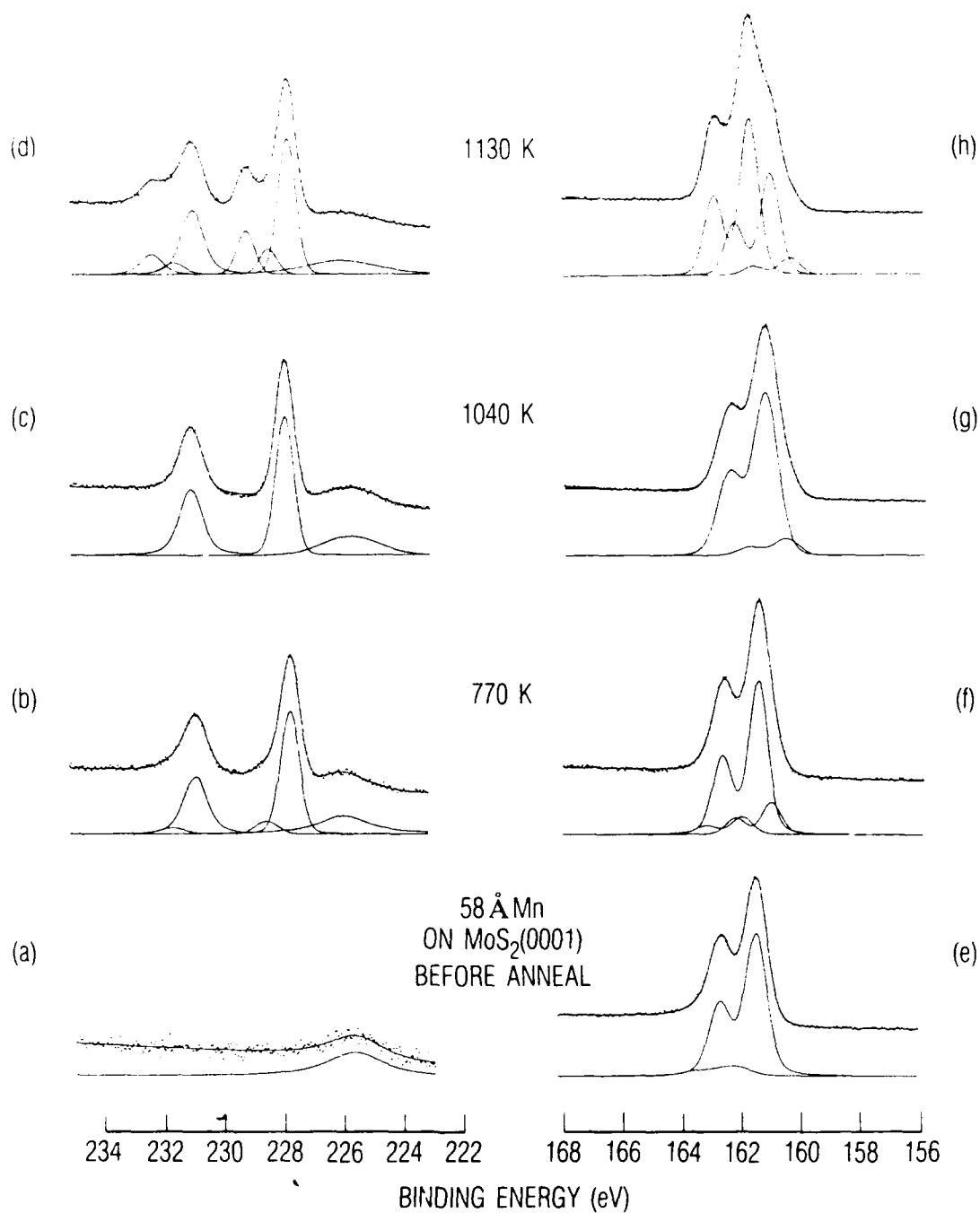


Fig. 3. Mo-3d (a-d) and S-2p (e-h) Core Level Spectra for Annealing of Mn on the MoS<sub>2</sub>(0001) Surface. Spectra were taken with same photon energies as in Fig. 1. Spectra are shown for (a,e) the 58 Å Mn film, and after annealing this film to (b,f) 770 K, (c,g) 1040 K, and (d,h) 1130 K. The S-2s peak is at ~226 eV in spectra a-d. Binding energies are relative to E<sub>F</sub>.

The drop in the Mo(metal) peak area as the annealing temperature is increased from 770 K to 900 K is due to continued MnS formation (see Section III-B, below), which competes with the Mo(metal) for coverage of the surface. The loss of some of the adsorbed S at this point may also be related to the formation of MnS. The increase in the Mo(metal) peak area between 900 K and 1040 K may be due to partial decomposition of the MnS, which serves as a source for the return of the adsorbed S. S adsorbed on Mo is relatively refractory<sup>19</sup> and, therefore, would not be desorbed at this temperature.

#### B. VALENCE BAND SPECTRA

Valence band photoelectron spectra were taken for photon energies of 152 eV and 225 eV during deposition of Mn on MoS<sub>2</sub>(0001) and subsequent annealing of the samples. Only the 152 eV spectra are reproduced here (see Fig. 4), since the results of the two sets show good agreement. Initial deposition causes shifting of the spectrum -0.3 eV to lower binding energy (see Fig. 4b), in agreement with the band-bending seen in the core levels. Also, increased intensity from 1 eV to the Fermi level indicates that the surface is becoming metallic due to the presence of metallic Mn. The MoS<sub>2</sub> peak structure is still seen in the 10 Å spectrum, showing that the substrate has not reacted appreciably or been covered by the overlayer. Also, when the metallic edge of the 10 Å spectrum is scaled to coincide with the corresponding metallic edge of the 35 Å spectrum, and the 35 Å spectrum is subtracted from the 10 Å spectrum, the resultant difference spectrum is virtually identical to that for the clean surface, indicating that the reacted layer (i.e., Mn+MnS+Mo) coexists with relatively undisturbed substrate. Therefore, probably no Mn<sub>x</sub>MoS<sub>2</sub> compound is formed during deposition. Spectra c and d in Fig. 4 (especially d) correspond well with the valence band spectrum for Mn metal.<sup>15</sup> The 35 Å spectrum (Fig. 4c) exhibits a bit more intensity in the areas of -4 eV and -6 eV than the 58 Å spectrum (Fig. 4d). This is due to the persistence of the signal from the substrate (compare Fig. 2, spectra c and d).

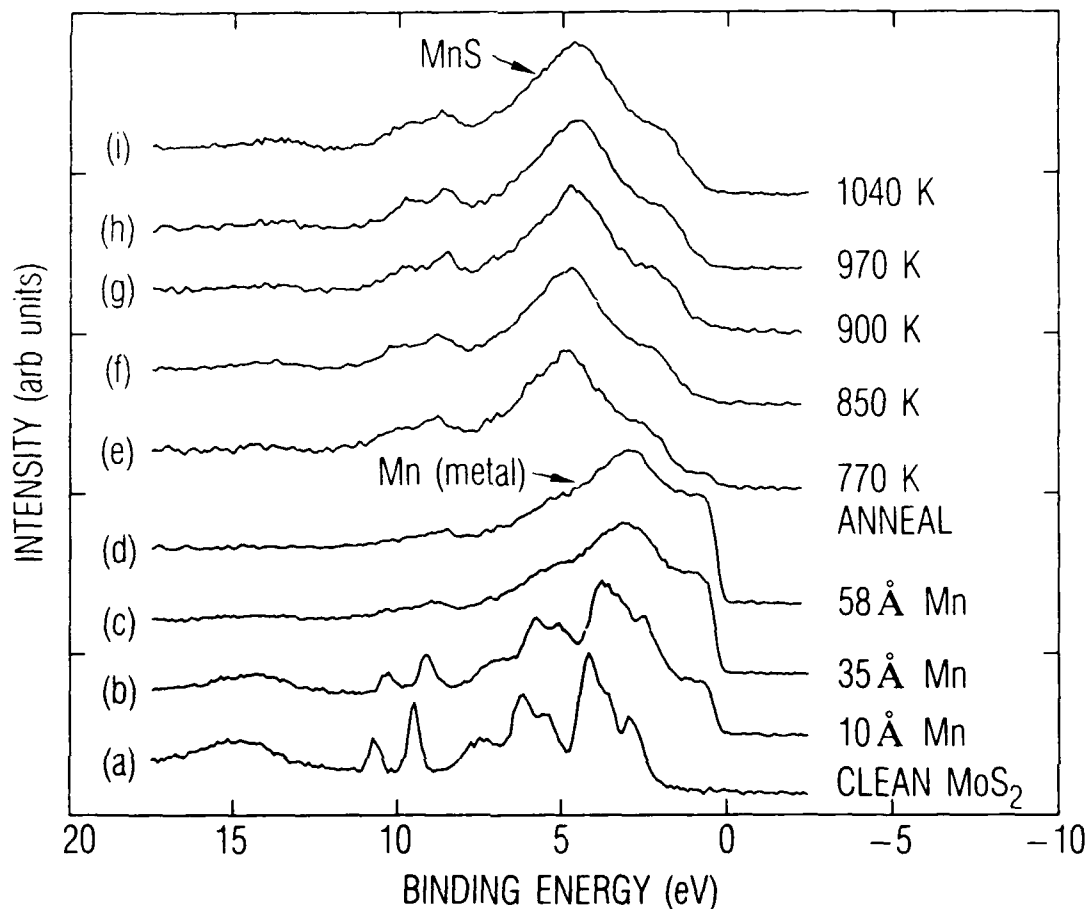


Fig. 4. Valence Band Spectra ( $h\nu = 152$  eV) for Deposition and Annealing of Mn on the MoS<sub>2</sub>(0001) Surface. Spectra are shown for (a) the clean MoS<sub>2</sub>(0001) -  $7 \times 1$  surface, and after deposition of (b) 10 Å Mn, (c) 35 Å Mn, and (d) 58 Å Mn. Spectra for the 58 Å Mn film are shown after annealing to (e) 770 K, (f) 850 K, (g) 900 K, (h) 970 K, and (i) 1040 K. The two peaks visible at ~9-11 eV result from the S-2p core level doublet produced by second-order light from the monochromator. Binding energies are relative to  $E_F$ .

With the anneal to 770 K (see Fig. 4e), a large increase in intensity appears at  $-5$  eV, due to the formation of MnS (see below) and the reappearance of the substrate. Also, the Mn metal areas of the valence band (at  $-1$  and  $-3$  eV) persist, indicating that there is a small amount of unreacted Mn at this annealing temperature. After annealing to 850 K, however, there is no evidence for the existence of unreacted Mn (see Fig. 4f). The spectra for anneals between 850 and 1040 K indicate a mixture of MnS (represented mainly by the peak at  $-5$  eV<sup>15,16</sup>) and metallic Mo (peak at  $-2$  eV<sup>20</sup>), in agreement with the core level spectra (see Fig. 2, spectra f and g; also Fig. 3, spectra c and g). The MnS peak shifts  $-0.5$  eV to lower binding energy as the temperature is increased from 900 K to 1040 K. This may be due to a phase transition in MnS from the  $\alpha$  phase to the  $\beta$  phase<sup>21</sup> or partial decomposition, as mentioned above.

#### C. FORMATION OF MoS<sub>2</sub>(0001) - 2 × 2

After annealing to 1130 K, the substrate (0001) - 1 × 1 LEED pattern reappeared, and also exhibited half-order spots over much of the sample surface, indicating the formation of a surface structure with (0001) - 2 × 2 periodicity. In addition, the core level spectra exhibit large changes in shape (see Fig. 3, spectra d and h). The Mo-3d and S-2p core levels can be deconvoluted into three doublets each. The Mo-3d spectrum (see Fig. 3d) exhibits the reappearance of the Mo(substrate) doublet resulting from MoS<sub>2</sub>, coexisting with a large Mo(metal) doublet. In addition, a smaller doublet appears with a binding energy intermediate between these two doublets, which probably represents the 2 × 2 regions of the surface. The S-2p doublet deconvolutes into a large substrate doublet, followed at lower binding energies by a slightly smaller S(MnS) doublet, and a small, lower binding energy doublet. As mentioned above, this lower binding energy doublet might represent adsorbed S, or it might represent S in the 2 × 2 regions of the surface.

Preliminary studies involving the thermal decomposition of the MoS<sub>2</sub>(0001) - 1 × 1 surface<sup>22</sup> correlate well with the present results. Annealing to temperatures in excess of 1375 K caused the formation of a

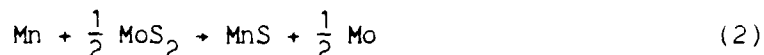
(0001) -  $2 \times 2$  LEED pattern, similar to annealing the Mn/MoS<sub>2</sub>(0001) interface to 1130 K in the present study. In addition, the core-level photoelectron spectra of the annealed MoS<sub>2</sub>(0001) surface appear similar to those of the annealed Mn/MoS<sub>2</sub>(0001) interface.

In a recent study of the Fe/MoS<sub>2</sub>(0001) interface,<sup>1</sup> a (0001) -  $2 \times 2$  LEED pattern was observed when the sample was annealed to 1200 K. This result, the results of the present study, and the preliminary thermal decomposition results for the clean surface, indicate that the (0001) -  $2 \times 2$  LEED pattern seen for higher temperature-annealed metal/MoS<sub>2</sub> interfaces is not due to the formation of a (metal)<sub>x</sub>MoS<sub>2</sub> compound, but rather is due to sulfur vacancy defects in the surface region, produced when the metals react with the MoS<sub>2</sub> to form metal-sulfur compounds. Therefore, these chemically produced defects allow the (0001) -  $2 \times 2$  structure to form at a lower temperature than for the clean surface. In addition, the difference in reactivity between Fe and Mn affects the formation of this structure. Although Fe exhibits some evidence of reactivity with respect to MoS<sub>2</sub>(0001),<sup>1,4</sup> the reactivity is considerably less than for Mn on MoS<sub>2</sub>(0001).<sup>2</sup> Since there is less deficiency of S in the substrate surface for Fe/MoS<sub>2</sub>, a higher temperature (1200 K) is required to produce the (0001) -  $2 \times 2$  defect structure than for Mn (1130 K).

Although valence band spectra for the 1130 K anneal were not taken with a 152 eV photon energy as in Fig. 4, a spectrum with a 225 eV photon energy (not shown) was taken that exhibits a broad peak with maximum intensity at ~4.5 eV, and higher intensity at ~2 eV than in the previous spectra. The general shape of the spectrum indicates that Mo(metal) and MnS continue to cover some of the surface, with a broad structureless valence band shape indicating disorder in the uncovered areas of the surface that contributed to the (0001) -  $1 \times 1$  and -  $2 \times 2$  LEED patterns.

#### IV. SUMMARY AND CONSLUSIONS

A core level and valence band photoelectron spectroscopy study was conducted of the Mn/MoS<sub>2</sub>(0001) interface. In general, it was shown that Mn reacted with the MoS<sub>2</sub>(0001) surface as represented in the overall reaction:



Specifically, Mn forms three-dimensional islands on MoS<sub>2</sub>, covering the substrate with a complete layer only for an amount of Mn that would have given a thickness equivalent to ~50 Å for layer-by-layer deposition. Reaction (2) initiated for thicknesses  $\lesssim 10$  Å Mn, and was driven by increasing amounts of Mn. The binding energies of the deposition-produced species in the Mn-3p and S-2p core level spectra corresponded to MnS, while the Mo-3d spectra indicated the formation of metallic Mo. Valence band spectra showed that for initial deposition, the partially reacted layer (i.e., Mn+MnS+Mo) formed an abrupt interface with the unreacted substrate.

The reaction was driven by annealing ~50 to ~58 Å Mn films on MoS<sub>2</sub>(0001) to temperatures in the range 770 - 1040 K. Analysis of the core levels after annealing to 770 K indicated that the MoS<sub>2</sub> substrate surface was sulfur-deficient, while valence band spectra showed that some unreacted Mn coexisted with a mostly MnS overlayer. The reaction was driven to completion by annealing to temperatures  $\gtrsim 850$  K.

Annealing to temperatures  $\gtrsim 1130$  K resulted in the formation of a MoS<sub>2</sub>(0001) - 2 × 2 LEED pattern. The observation of this surface structure is interpreted in terms of a sulfur-vacancy-produced defect structure, rather than a metal-Mo-S compound.

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Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, chemical dynamics, environmental chemistry, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed chemical and excimer laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, sensor out-of-field-of-view rejection, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photo-sensitive materials and detectors, atomic frequency standards, and environmental chemistry.

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Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices; atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; non-destructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.